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THE EFFECT OF D STAGE REACTION TIME ON THE CHARACTERISTICS OF WHOLE EFFLUENTS AND EFFLUENT FRACTIONS FROM D(EO) BLEACHING OF OXYGEN DELIGNIFIED SOFTWOOD KRAFT PULP

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ABSTRACT

The effect of D stage reaction time on the characteristics of effluents and effluent fractions from D(EO) bleaching of oxygen delignified softwood kraft pulp is considered in this paper. Effluents from the OD(EO) sequence with D stage reaction times of 3 seconds, 1 minute, 5 minutes, and 30 minutes were fractionated and characterized. The fractionation consisted of ether extraction and separation of the extract into acidic, phenolic, and neutral subfractions. Adsorbable organic halide (AOX) and total organic carbon (TOC) were determined for the whole D and (EO) effluents as well as for the fractions from each stage. Each fraction was characterized in terms of its chlorine to carbon ratio (expressed as the number of chlorine atoms per hundred carbon atoms, Cl/C_{100}) and in terms of the proportions of the total TOC and AOX contained within it.

A D stage of only 3 seconds duration resulted in 67% of the delignification achieved in a 30-minute stage. The 3-second D stage resulted in only 26% as much AOX and 34% of the Cl/C_{100} given by the 30-minute D stage. A 1-minute D stage achieved 84% of the delignification while generating only 42% of the AOX and 51% of the Cl/C_{100} of the 30-minute stage.

The Cl/C_{100} of all effluent fractions except the neutral fraction was reduced when the D stage was shortened from 30 minutes to 3 seconds. The extent of this reduction was different for the different fractions. In addition to a sharp Cl/C_{100} reduction in the environmentally significant ether soluble fraction, the proportion of ether soluble TOC was reduced at short D stage reaction times, and the proportion of the total AOX found in the ether soluble fraction reached a minimum value at 1 minute of D stage reaction time. These effects are primarily due to the acid subfraction of the ether soluble material. A bleaching sequence with a very short D stage or a low kappa factor D stage may therefore possess environmental advantages in addition to an overall AOX reduction.

INTRODUCTION

In the area of pulp bleaching, environmental issues continue to gain importance relative to more conventional concerns such as efficiency of delignification and economics. The threat of extremely low AOX limits and consumer demand have already led many mills to substantially reduce their AOX discharge by a variety of methods including improved brownstock washing (1-3), extended Kraft delignification (4-6), oxygen delignification (1, 4, 7, 8), substitution of chlorine dioxide for chlorine (4, 7, 9-14), and oxidative caustic extraction (9, 15-17).

Although these methods reduce AOX, it remains uncertain what effect they have on the environment, because AOX reduction does not necessarily mean the environmental impact is reduced (18, 19). On the other hand, it may be somewhat irrelevant whether AOX reduction actually affects the environment, due to impending regulation.

Levels of AOX in proposed regulations may not be achievable using chlorine containing bleaching agents. However, both chlorine dioxide bleaching and oxygen delignification offer more environmental benefits over conventional chlorine bleaching than the AOX reduction alone suggests (20). Since conversion to totally chlorine free bleaching processes is not yet a viable alternative for most pulp producers, bleaching with chlorine dioxide is worth further study. If such a system can be optimized with respect to certain process variables, perhaps the required AOX reduction may be achieved and the environmental effects of the sequence minimized as well. The effect of D stage pH on the characteristics of whole effluents and effluent fractions from D(EO) bleaching of oxygen delignified softwood kraft pulp has been previously investigated (21) using an effluent fractionation based on ether extraction (20).

Another D stage process variable which may be expected to impact the nature of the effluent is reaction time. Removal of lignin and substitution on organic material by chlorine during chlorine dioxide treatment would be expected to have different time de-

pendence, since the two processes occur by different mechanisms (22, 23). A variety of bleaching studies have considered the effect of reaction time on lignin removal in the chlorination of kraft pulps (24-30), in the chlorine dioxide prebleaching of kraft pulps (31), and in the prebleaching of kraft pulps with combinations of chlorine and chlorine dioxide (32, 33). However, none of these studies considered the effect of reaction time on the nature of the effluents.

Pulp bleaching effluents in general have been characterized with respect to adsorbable organic halide (AOX) (34-38) and in terms of individual compounds or environmentally significant groups of compounds such as chlorophenolics (34, 39-46), chlorinated dioxins (43, 47, 48), chlorinated neutral compounds (46, 49, 50), chlorinated carboxylic acids (46, 51), and chloroform (42, 52). However, because of the complexity of pulp bleaching effluents, these analyses give an incomplete picture of their likely environmental effects.

A preferable alternative is summative analysis of the effluent by fractionation into meaningful classes of compounds, followed by relevant characterization of the fractions. One such procedure, based on ether extraction, has been developed and applied to effluents (20, 21). Ether extraction was chosen as the basis for this procedure because virtually all effluent components known to be significant from an environmental standpoint are found in the extracts. For example, the ether extract contains low molecular weight material (53, 54) which may correlate with acute and chronic toxicity (19, 55, 56). The ether extract exhibits most of the effluent's mutagenicity (49, 57, 58) and toxicity (53) and contains environmentally significant compounds such as chlorophenolics (44, 59) and chlorinated neutral compounds (50, 60). Chlorine to carbon ratios (expressed as the number of chlorine atoms per hundred carbon atoms, Cl/C_{100}), which may be expected to correlate with environmental behavior, were determined for the fractions. Within certain effluent fractions, the ratio of chlorine to carbon atoms may predict acute toxicity (39, 59), chronic toxicity (61), and lipophilicity (62). These fractionation and characterization methods were used for the present study of the effect of D stage reaction time on D(EO) bleaching of oxygen delignified softwood kraft pulp.

EXPERIMENTAL APPROACH

Pulp Bleaching

A mill-produced, oxygen-bleached kraft pulp with a kappa number of 14.1 was bleached by a D(EO) sequence in the laboratory. D stage reaction times of 3 seconds, 1 minute, 5 minutes, and 30 minutes were considered. The D stages were quenched with excess sodium sulfite after the appropriate bleaching time. Only the first two stages of bleaching were done, since most of the delignification and therefore most of the effluent load production occurs in these stages. The D stages were done in a specially designed batch reactor, and the (EO) stages were done in a high shear mixer. Kappa numbers after bleaching are given in Table I.

A schematic diagram of the D stage bleaching reactor used in this study is given in Figure 1. The reactor was specially designed to bleach pulp for short periods of time, to quench the reaction after a given time interval, and to produce sufficient quantities of effluent for analysis. Using this reactor, bleaching at 2% consistency and with a D stage reaction time as short as 3 seconds has been done.

The reactor consists of a thermostatted 20 L cylindrical reaction chamber with chemical injection cylinders on 3 sides of it. During a typical bleaching experiment, only two of the injection cylinders were used: one for the bleaching agent and one for the quench. During such experiments, a pulp slurry of the appropriate consistency, pH, and temperature is put in the mixing chamber. The mixing chamber is initially separated from the injection cylinders by teflon rupture membranes. The cover, equipped with a teflon-coated mixer, is attached and the chemicals added to the cylinders. Once the pulp is mixing at 350 rpm, the bleaching agent is injected, through the membrane by an air-driven piston, into the slurry. At this point, the consistency is 2%. The injection of chlorine dioxide triggers a timing mechanism which automatically injects the quench after the appropriate time.

Based on work by Liebergott and co-workers (27), the mixing rate of 350 rpm should be sufficient to ensure uniform bleaching with aqueous bleaching agents. Data showing no effect of mixing on reaction rate (27, 29) suggest that bulk phase diffusion does not limit the reaction rate. During a preliminary mixing study done at only 250 rpm, high-speed videotape demonstrated that complete mixing in about 0.5 seconds.

Effluent Fractionation and Characterization

The effluents produced in this study were fractionated by ether extraction. To measure Cl/C_{100} on the ether extract and its fractions, the ether was exhaustively removed by evaporation, and AOX and TOC were then measured on each fraction. During evaporation, volatiles other than ether were also removed. To obtain information on the volatile fraction, a sample of the whole effluent was similarly evaporated and the carbon and chlorine losses determined.

Figure 2 depicts the effluent fractionation scheme, and Table II lists the names or codes of all effluent fractions and provides an explanation of each. The bleaching effluents were extracted with ether in continuous liquid-liquid extractors. Two successive extractions were performed, resulting in three fractions: a non-extractable fraction and two ether extractable fractions. The first ether fraction is the most nonpolar of the extractable material and is readily extracted, while the second is more polar and is removed slowly over an extended period. The first ether fraction was further separated into acids, phenolics, and neutrals. Each fraction was then evaporated, as represented in Figure 2 by the dashed horizontal lines, to yield the final samples.

Data Analysis

The different D stage reaction time bleaching experiments were performed in duplicate, and the effluents from the D and (EO) stages of bleaching were fractionated and analyzed separately. This resulted in two completely independent sets of data for each D stage reaction time.

Analyses of variance (AOV) were done on the data from each fraction to assess the significance of differences between D stage reaction times and between stages. Since data with high Cl/C_{100} had a greater variance than the low Cl/C_{100} data, all Cl/C_{100} data were log transformed to stabilize variance. When AOV showed a significant reaction time effect, a least significant difference was determined using Duncan's multiple range test (63).

RESULTS AND DISCUSSION

The data for the whole effluents and for all fractions are given in Tables III-X. The total TOC and AOX (given in Table III) represent TOC and AOX mass balances around the fractionation scheme, and were determined as the sums of the AOX and TOC measurements for the neutral, phenolic, acidic, polar, hydrophilic, and volatile fractions.

Data for the pulp delignification and for the whole effluent and effluent fraction characteristics are presented graphically in Figures 3 through 16. Effluent characterization graphs consist of 3 curves based on data collected at the 4 different D stage bleaching times of 3 seconds, 1 minute, 5 minutes, and 30 minutes. The curves labeled D stage refer to the D stage effluent alone, and the curves labeled (EO) stage refer to the (EO) stage effluent alone. The curves labeled D + (EO) stage refer to the combined data from the D and (EO) stages, not to measurements on combined filtrates. The D, (EO), and D + (EO) designations apply to the data tables as well.

The data for individual fractions were interpreted in terms of their Cl/C_{100} values and their relative sizes, expressed as a percentage of total TOC or AOX. The Cl/C_{100} is of interest as a likely predictor of lipophilicity and toxicity within certain fractions.

Degree of Delignification

The effect of D stage reaction time on delignification (expressed as DE Kappa number) is shown in Figure 3, and the data are given in Table I. D stage bleaching for only 3 seconds results in a Kappa number decrease from 14.1 to about 7.8, or 67% of the Kappa number reduction that occurs in 30 minutes. One minute of D stage bleaching results in about 84% of the total 30-minute kappa number reduction, or a DE Kappa number of about 6.2. This shows that in conventional bleaching the greater part of the lignin is made soluble after only a very short time, and undergoes further reaction with chlorine containing chemicals for an extended period. This results in increased chlorine substitution on the organics as reaction time increases.

In addition to the kappa number data, Table I shows the sum of the TOC values for the D and (EO) effluents and the TOC per unit of Kappa number decrease, for the different D stage reaction times. Although at 3 seconds the mean $TOC/\Delta Kappa$ is higher than at the other D stage times, the difference is not large enough to be considered statistically significant.

Whole Effluents

Data for the whole effluents are presented in Table III. The whole effluents contain 2.2-7.0 kg/t TOC and

0.04-0.40 kg/t AOX, depending on the stage and on the D stage reaction time.

Figure 4 shows the effect of D stage reaction time on effluent TOC content. The D stage TOC and the overall D + (EO) stage TOC increase with increasing reaction time. The (EO) stage TOC remains relatively constant at all reaction times. The D stage effluent TOC formation and the Kappa number reduction are virtual mirror images (Figure 5) indicating that the increased delignification seen at longer reaction times is due to increased D stage delignification, not (EO) stage delignification.

The amount of (EO) stage TOC formed at 3 seconds is almost identical to the amount formed at 30 minutes of D stage reaction time. This indicates that lignin removal in the latter part of the D stage and (EO) stage lignin removal may be parallel reaction sequences operating independently rather than sequential reactions, since after 3 seconds D stage reaction time has little or no effect on (EO) stage delignification.

Figure 6 shows the effect of D stage reaction time on the whole effluent Cl/C_{100}. While 67% of the delignification is seen after 3 seconds in the D stage, the overall Cl/C_{100} in the effluent is only about 34% of that seen after 30 minutes of D stage bleaching. AOX produced with the 3-second D stage is only 26% of that produced using a 30-minute D stage. Similarly, a 1-minute D stage achieves 84% of the delignification while generating only 42% of the AOX and 51% of the Cl/C_{100} of the 30-minute stage. Short reaction times favor lignin removal over substitution of chlorine atoms onto organic material. The whole effluent Cl/C_{100} approaches an asymptotic level as D stage reaction time increases.

Ether Soluble Fraction

Table IV presents detailed data for the ether soluble fraction. It contains 0.2-0.9 kg/t TOC, representing 7-20% of the total TOC, and 0.01-0.10 kg/t AOX, representing 14-36% of the total AOX. The ether soluble fraction contains low molecular weight compounds that are nonpolar in nature.

The mean ether soluble TOC, expressed as a percentage of the total TOC, is shown in Figure 7 for all D stage reaction times. For both the D and (EO) stage effluents, a greater proportion of the TOC is ether soluble when the D stage is 30 minutes long than when it is of short duration. Increased reaction time may allow further fragmentation of already solublized lignin, resulting in a lower molecular weight material and more ether soluble TOC. Although the D stage effluent appears to have a maximum proportion of ether soluble TOC at 1 minute of reaction time and the (EO) stage effluent a minimum, the overall D + (EO) proportion of ether soluble TOC increases to an asymptotic level with increased D stage reaction time.

Figure 8 shows the ether soluble Cl/C_{100} for the different D stage reaction times. Increased D stage reaction time generally results in increased Cl/C_{100} in the ether soluble fraction for both stages. Increased levels of chlorine substitution and associated decreases in water solubility may be responsible, in part, for the increase in the size of the ether soluble fraction at longer D stage reaction times. After 3 seconds of D stage bleaching, the overall D + (EO) Cl/C_{100} value is only about 38% of its value at 30 minutes, although about two-thirds of the delignification occurs. A 1-minute D stage results in only 29% of the ether soluble AOX and 43% of the Cl/C_{100} of the 30-minute D stage, yet 84% of the delignification is done.

The proportion of ether soluble AOX present in the effluents produced by the various D stage reaction times is shown in Figure 9. A minimum proportion of ether soluble AOX (presumed to be "bad" AOX) occurs in effluents produced using the 1-minute D stage. A similar trend is evident in both the D and (EO) stage effluents.

Within the ether soluble fraction, a reduced D stage reaction time may have several benefits of an environmental nature: a substantially reduced Cl/C_{100} for the ether soluble material, a reduced proportion of ether soluble TOC, and a minimum proportion of ether soluble AOX. Based on these results, the potential environmental effects of the OD(EO) sequence may be minimized by running the D stage for 1 minute or less.

Polar Fraction

Detailed results for the polar fraction, or that material which is extracted slowly by ether, are shown in Table V. The phenolic fraction contains 0.1-0.8 kg/t TOC or 4-12% of the total TOC, and 0.002-0.04 kg/t AOX or 3-15% of the total AOX. The material contained within this fraction is likely to be low molecu-

lar weight and more polar than that within the ether soluble fraction.

Although no increase in the proportion of polar TOC is seen as D stage reaction time increases, the Cl/C_{100} increases at longer reaction times, as shown in Figure 10. At 3 seconds, the overall D + (EO) polar Cl/C_{100} is only about 19% of that which occurs at 30 minutes.

Hydrophilic Fraction

Complete data on the hydrophilic fraction are given in Table VI. The fraction contains 2-5 kg/t TOC (70-85% of the total TOC) and 0.03-0.16 kg/t AOX (41-77% of the total AOX). Material within the hydrophilic fraction is either very polar or of high molecular weight relative to the extractable fractions.

No trend in the proportion of TOC within this fraction is seen with increasing D stage reaction time. However, the Cl/C_{100} increases at longer D stage reaction times, as shown in Figure 11. The overall D + (EO) hydrophilic Cl/C_{100} is only 36% of its 30-minute value after 3 seconds of D stage reaction time.

It is interesting to note that both the polar and hydrophilic fraction D stage Cl/C_{100} values exhibit relative maxima at 1 minute of D stage reaction time, corresponding to the apparent minimum seen within the D stage ether soluble Cl/C_{100}. This is consistent with the steadily increasing whole D stage effluent Cl/C_{100} and lends additional credibility to the data.

Acid Fraction

Table VII presents the detailed results for the acid subfraction of the ether soluble material. About 0.15-1.2 kg/t TOC, representing 6-18% of the total TOC, and 0.006-0.10 kg/t AOX, representing 12-31% of the total AOX, is contained within this fraction. The acid fraction is likely to include both chlorinated and nonchlorinated resin acids, fatty acids, benzoic acid derivatives, and various mono- and dibasic carboxylic acids.

Increased D stage reaction time generally results in an increased proportion of acidic ether soluble TOC, as shown in Figure 12. The increased proportion of ether soluble TOC (shown previously) is accounted for by the acid fraction, since the proportions of phenolic and neutral TOC do not change with D stage reaction time.

The acid fraction Cl/C_{100} increases to an asymptotic level with D stage reaction time, as shown in Figure 13. The overall Cl/C_{100} at 3 seconds is only 30% of that at 30 minutes. The minimum in the proportion of ether soluble AOX is also likely to be due to the acid fraction's contribution to the ether soluble material. Figure 14 shows an apparent minimum proportion of acid fraction AOX at 1 minute of D stage reaction time, as was seen for the ether soluble fraction.

A reduction in D stage reaction time appears to have several benefits within the acid fraction: a substantially reduced Cl/C_{100}, a reduced proportion of acid fraction TOC, and a minimum proportion of acid fraction AOX. Although the acid fraction is not considered the most potentially harmful subfraction of the ether soluble material since it is the most polar portion, it is nevertheless the largest component of the environmentally significant ether soluble fraction, and improvements within this fraction are therefore of interest.

Phenolic Fraction

Complete data for the phenolic fraction are shown in Table VIII. The fraction contains 0.02-0.06 kg/t TOC or 0.6-1.0% of the total TOC, and 0.001-0.003 kg/t AOX or 0.9-2.3% of the total AOX. The phenolic fraction is likely to contain both chlorinated and nonchlorinated phenols, guaiacols, vanillins, and other degradation fragments with phenolic functionality.

The duration of the D stage does not affect the proportion of phenolic TOC. On the other hand, the Cl/C_{100} of this fraction increases with D stage reaction time as shown by Figure 15. The effect appears to be smaller in the phenolic fraction than in the other fractions (for example the acid fraction) since the phenolic Cl/C_{100} reaches an asymptotic level at a shorter D stage reaction time. The overall reduction in the extent of the Cl/C_{100} from 30 minutes to 3 seconds (49%) is less in this case, but still an important reduction since this is an environmentally significant fraction.

Neutral Fraction

Table IX presents the entire data set for the neutral fraction of the ether soluble material. This fraction contains 0.02-0.06 kg/t TOC (0.4-4.8% of the total TOC) and 0.0006-0.0030 kg/t AOX (0.8-2.4% of the total AOX). Contained within the neutral fraction are chlorinated and nonchlorinated thiophenes, benzene

derivatives, enollactones, furanones, pyrones, dimethyl sulfones, and various hydrocarbons.

The proportion of neutral fraction TOC is not affected by D stage reaction time. As shown by Figure 16, there is no clear reduction in neutral fraction Cl/C_{100} with reduced D stage reaction time as occurred in other fractions. However, the Cl/C_{100} at 1 minute is significantly reduced versus that at 5 minutes. This fraction was the most difficult to work with, because of its small size and hydrophobic nature. Consequently, the data exhibit considerable scatter. Nevertheless, it is very interesting that both the D and (EO) stage curves are nearly identical. The reproducibility of these graphs lends some credibility to the data within them.

Volatile Fraction

There are no significant time related effects observed in the volatile fraction data, due to scatter and incomplete data. The data set is included here (Table X) for the purposes of a complete analysis, however. Volatile compounds present may include chloroform, methanol, and acetic acid.

Practical Implications

A major practical implication of this work is that a sequence with a very limited D stage (3 seconds long) removes two-thirds of the material removed by a sequence with a 30-minute D stage, while reducing the D + (EO) stage AOX to only 26% of that formed by a sequence with a 30-minute D stage. Similarly, a 1-minute D stage results in 84% of the lignin removal with only 51% of the AOX production. Since (EO) stage lignin removal is unaffected by the extent of the D stage, limiting the D stage, either in time or perhaps in level of charge, may allow compliance with AOX regulation if the remaining lignin can be removed by other means. Possible methods of removal may be additional oxidative enhancement of the caustic extraction stages or a second, very limited chlorine dioxide delignification stage prior to brightening. A second delignification stage would have minimal impact on the effluent since most lignin is already removed, and a small ClO_2 charge would be applied. Concurrently with this work it has been shown that high brightness can be achieved, using the very limited kappa factor of 0.05 in the D stage (64). In this case, the stages after the D stage were strengthened to achieve supplemental delignification.

A second practical implication of this work is that such a limited D stage would require no bleach tower, simply a mixer and a length of pipe for retention. Since towers are not needed, an additional chlorine dioxide delignification stage could be installed at a much lower capital cost than a conventional stage.

EXPERIMENTAL METHODS

Pulp Bleaching

A mill-produced, 14.1 kappa O_2-delignified southern softwood kraft pulp was used in this study. The pulp was collected just after the O_2 stage and was well washed before bleaching.

D Stages

All D stages were done in a specially designed 20 L batch reactor. Bleaching was done at 2% consistency, at 45°C, and at a kappa factor of 0.25. The mixer was run at 350 rpm. Initial pH was adjusted to 2 by the addition of sulfuric acid solution. A 13 g/L solution of sodium sulfite was used for D stage quenching. After quenching with 1.5 L of the sulfite solution, the D stage slurry was at about 1.8% consistency.

(EO) Stages

All (EO) stages were done in a Quantum Technologies high shear mixer at 10% consistency, at 70°C, and for 70 minutes. The NaOH charge was 0.55 times the total active chlorine charge; the O_2 charge was 0.5% on pulp; and no carryover was added since it contained sodium sulfite . Addition of O_2 pressurized the mixer to about 20 psig. The slurry was mixed at 15 hertz for 3 seconds, every 5 minutes.

Effluent Preparation

The D stage effluent was collected by filtration of the 1.8% slurry; the (EO) stage effluent was similarly collected after the 10% slurry was diluted to 1.8%. This was done to maintain a similar TOC content in all effluents for ether extraction. Effluent samples were filtered to remove any fibers and acidified to a pH of less than 2. Ether extractions were always started within 2 days of effluent collection.

Ether Extraction of Effluents

Ether extraction was done on 4 L of effluent using continuous liquid-liquid extractors. Extraction was car-

ried out with 500 ml of diethyl ether. The first ether phase was collected after 96 hours of extraction and was replaced with 500 ml of fresh ether. Extraction was continued for 336 total hours. The extraction was then stopped, and the second ether phase and the non-extractable materials were collected.

Ether Extract Fractionation

The first ether phase was diluted to 500 ml, 100 ml of the sample collected, and the remaining ether placed in a separatory funnel for fractionation. The ether was extracted three times with 25 ml of 0.5 M $NaHCO_3$, and the extracts were collected and acidified. The ether was next extracted three times with 25 ml of 0.5 M NaOH, and these extracts were also collected and acidified. The $NaHCO_3$ soluble material is the acidic fraction; the NaOH soluble material is the phenolic fraction; and the remaining ether soluble material is the neutral fraction.

Sample Preparation

Ether was removed from all samples by evaporation on a rotary evaporator. A vacuum pump was applied to the evaporator containing the samples for a minimum of 3 hours. The samples were then acidified and diluted to a known volume. To ensure reasonable sample recovery and to be certain the ether was removed, TOC and AOX mass balances were done around the fractionation scheme.

TOC Analysis

Measurement of TOC was done using a Beckman model 915-B Tocamaster analyzer. The instrument was calibrated using standard solutions of potassium hydrogen phthalate. Samples were prepared for TOC analysis by acidifying them, and sparging for 5 minutes with nitrogen to drive off any interfering carbonate species.

AOX Analysis

Measurement of AOX was done using a Dohrman model DX-20 organic halide analyzer. Sample preparation was done by a modification of method SCAN-W 9:89 (54). After the initial adsorption on carbon, the filtrate was treated with a second batch of carbon to minimize "breakthrough." All samples were shaken for an hour, the carbon filtered, the filtrate collected, and more carbon added to this filtrate. This filtrate was treated identically to the first AOX batch.

SUMMARY AND CONCLUSIONS

A 3-second D stage in the OD(EO) bleaching of a softwood kraft pulp resulted in 67% of the delignification that occurred with the same sequence utilizing a 30-minute D stage. At the same time, the overall whole effluent Cl/C_{100} was reduced to 34% of its 30-minute value, while the overall D + (EO) stage AOX was reduced to 26% of the 30-minute AOX. A 1-minute D stage achieved 84% of the delignification while generating only 42% of the AOX and 51% of the Cl/C_{100} of the 30-minute stage. Additional reaction time provided limited delignification benefits, while increasing quite significantly the level of chlorine substitution on dissolved organics. Based on effluent TOC measurements, the (EO) stage delignification remained constant for all D stage reaction times.

With the exception of the neutral fraction, the Cl/C_{100} of all effluent fractions was reduced to varying degrees as the D stage reaction time was shortened. In the environmentally significant ether soluble fraction, in addition to a sharp reduction in the Cl/C_{100}, the proportion of ether soluble material was reduced for short D stage reaction times, and the proportion of ether soluble AOX (assumed to be "bad" AOX) reached a minimum under the 1-minute D stage conditions. These effects are likely to be caused primarily by the acidic fraction of the ether soluble material. In addition to reducing the overall effluent AOX, a bleaching sequence with a limited D stage may therefore represent environmental benefits in addition to the obvious reduction in total AOX.

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Figure 1. Top View Schematic Diagram of D Stage Batch Bleaching Reactor.

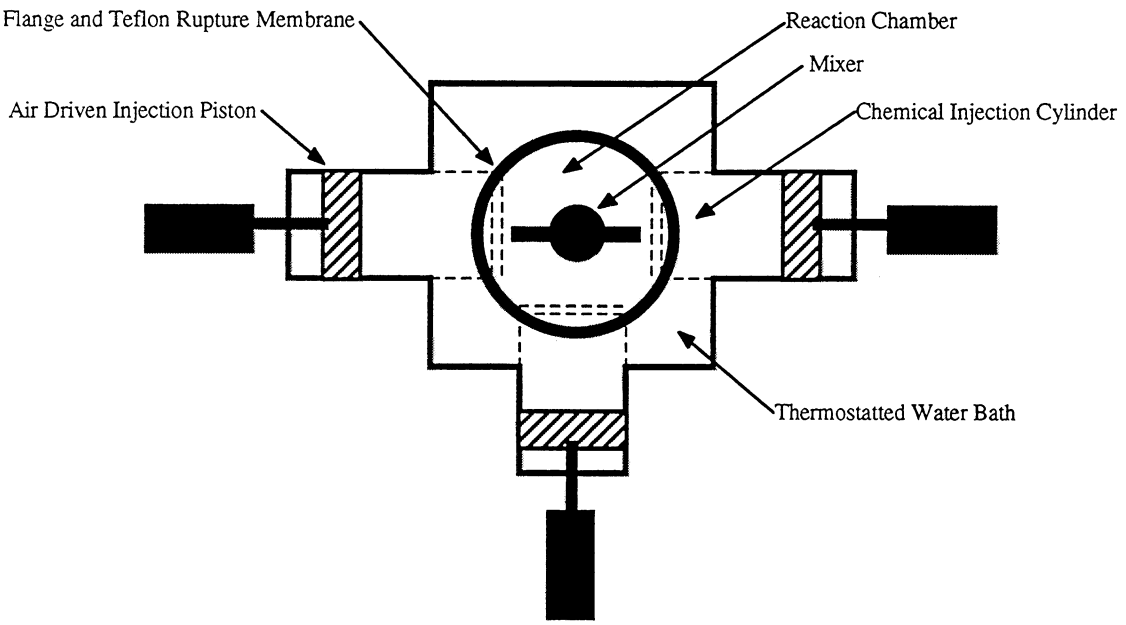
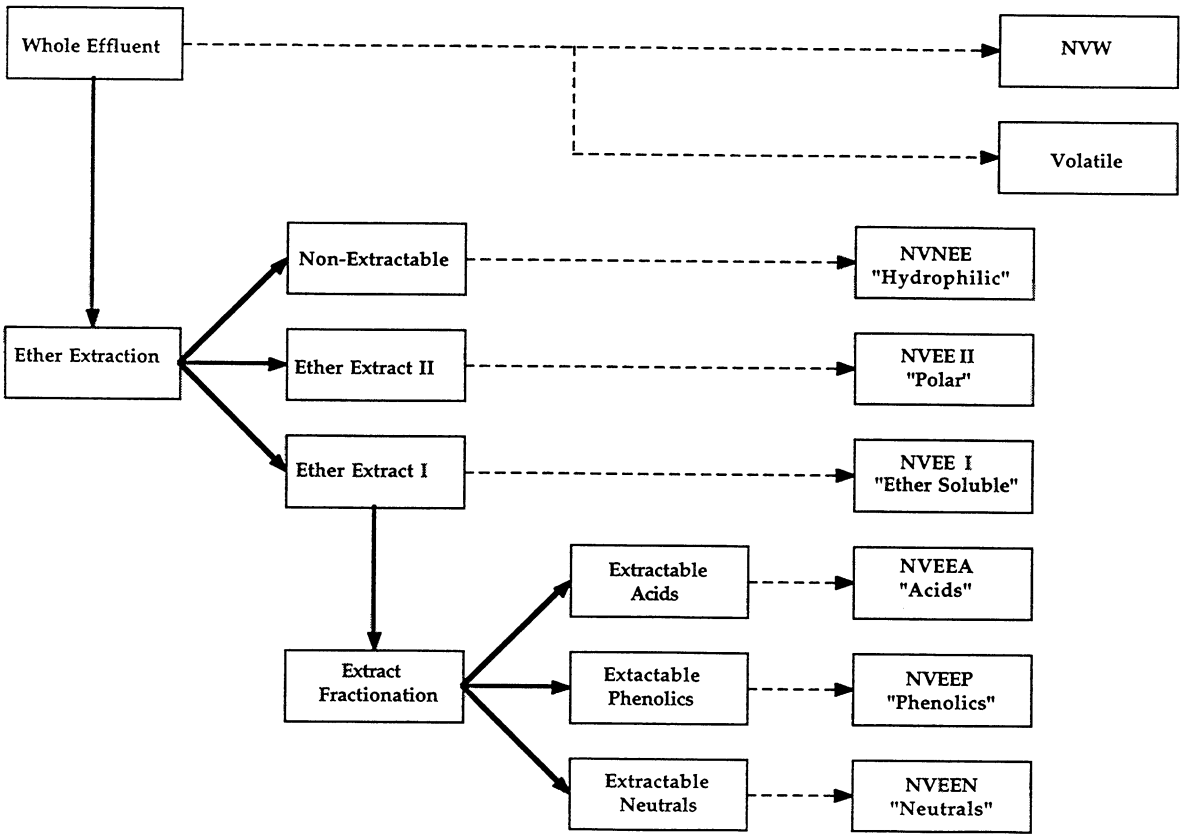


Figure 2. Effluent Fractionation.



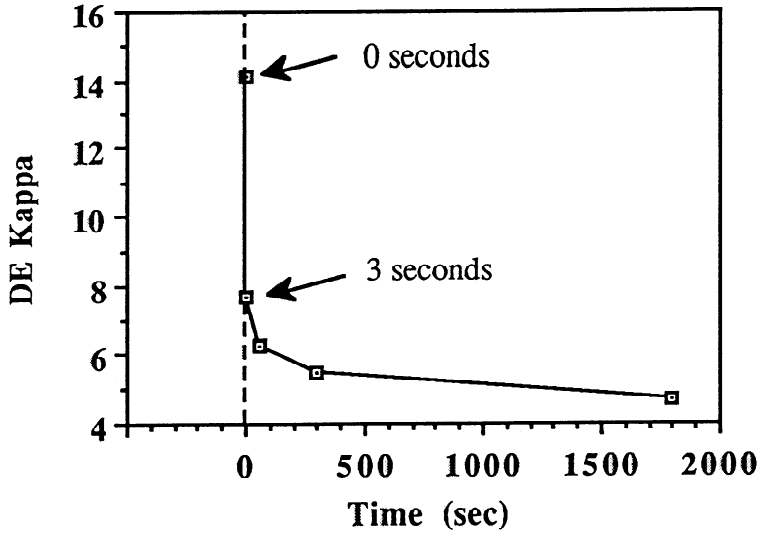


Figure 3. Pulp Delignification.

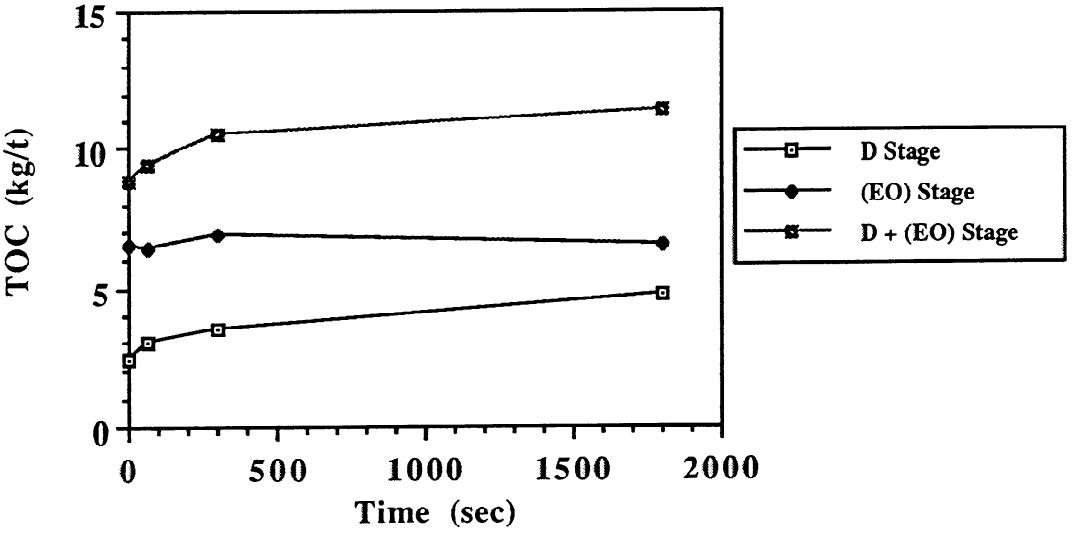


Figure 4. Whole Effluent TOC.

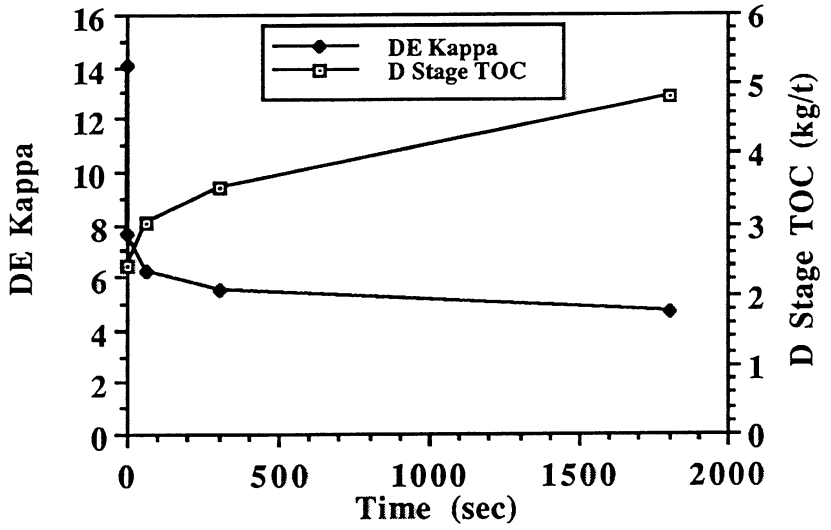


Figure 5. Kappa Numbers and D Stage TOC.

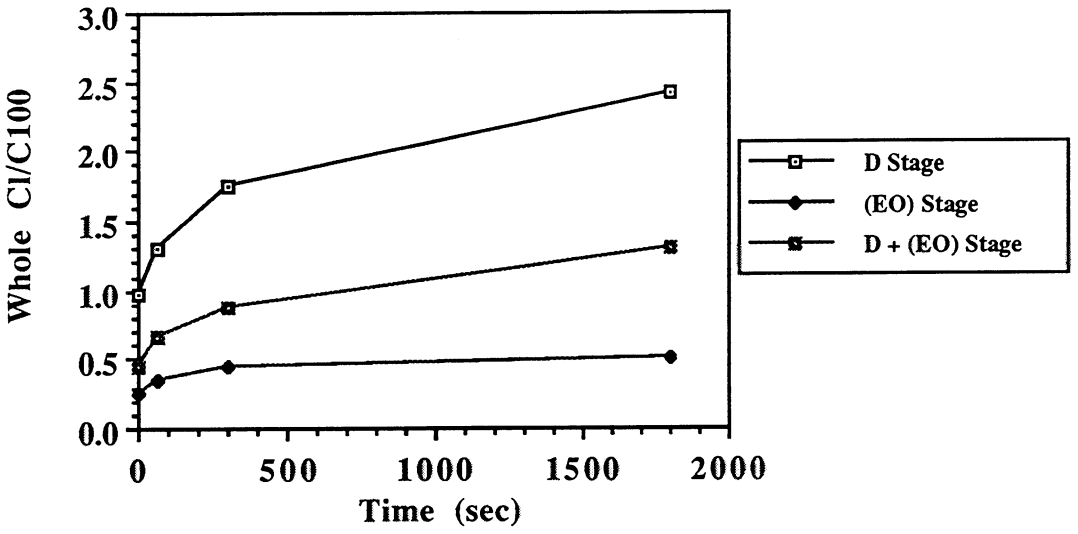


Figure 6. Whole Effluent Cl/C100.

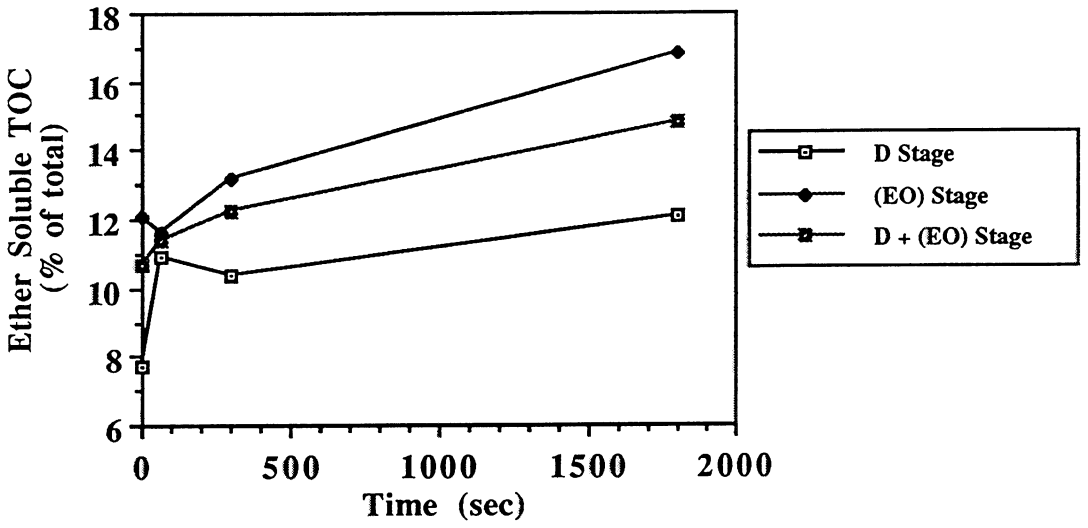


Figure 7. Ether Soluble TOC, as % of Total.

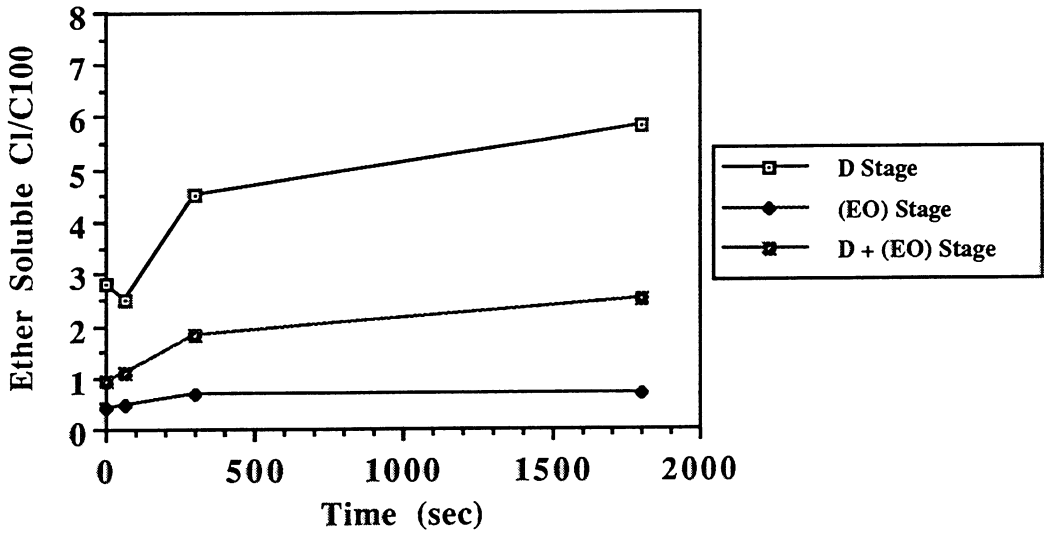


Figure 8. Ether Soluble Cl/C100.

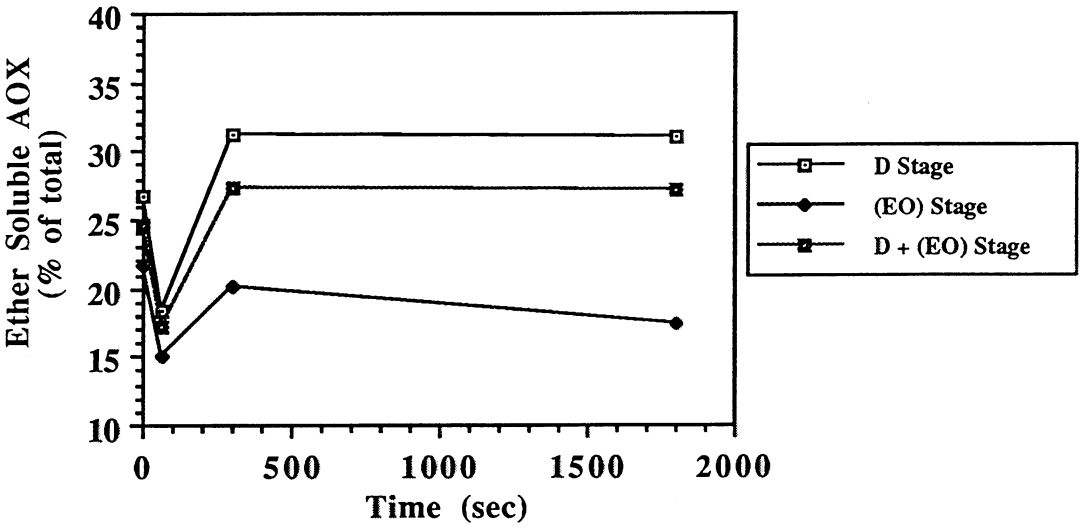


Figure 9. Ether Soluble AOX, as % of Total.

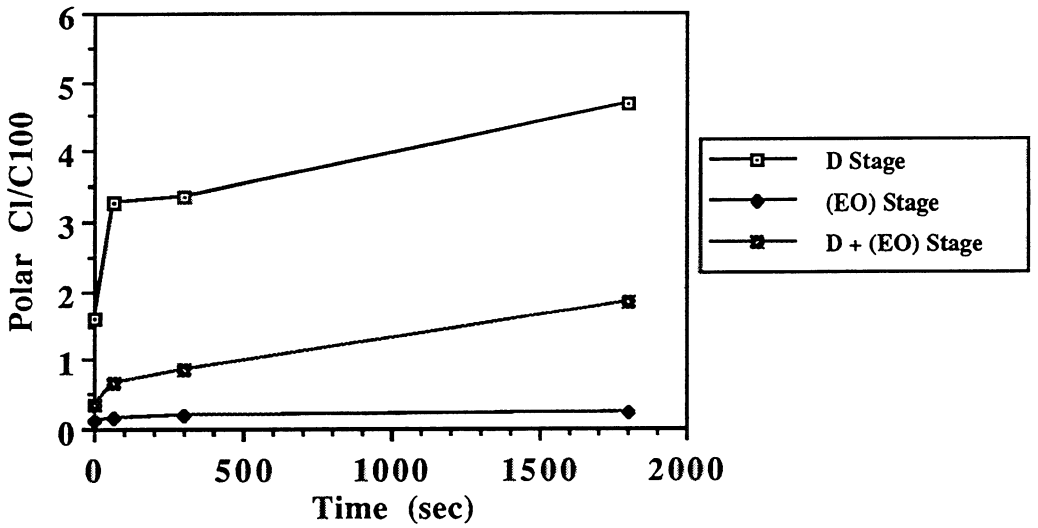


Figure 10. Polar Fraction Cl/C100.

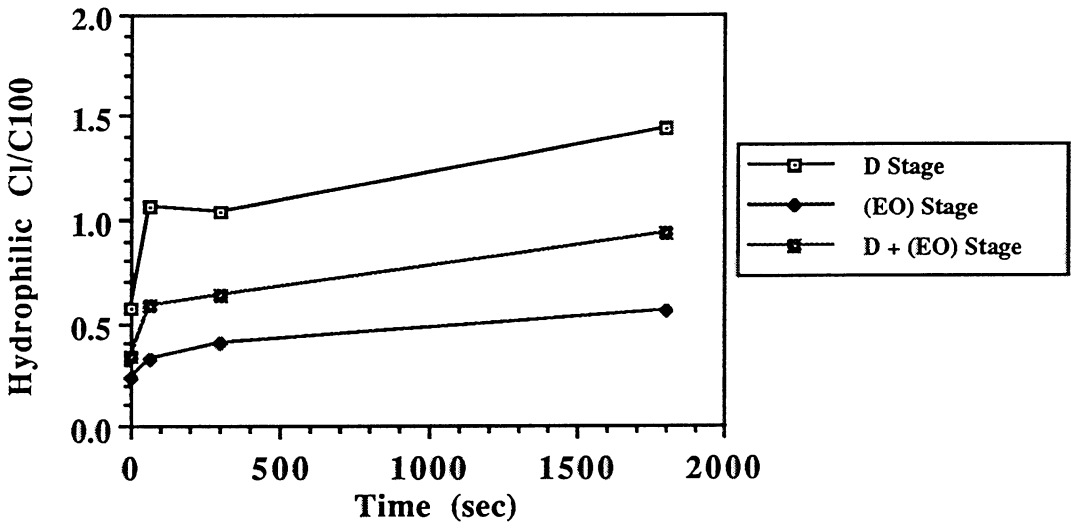


Figure 11. Hydrophilic Fraction Cl/C100.

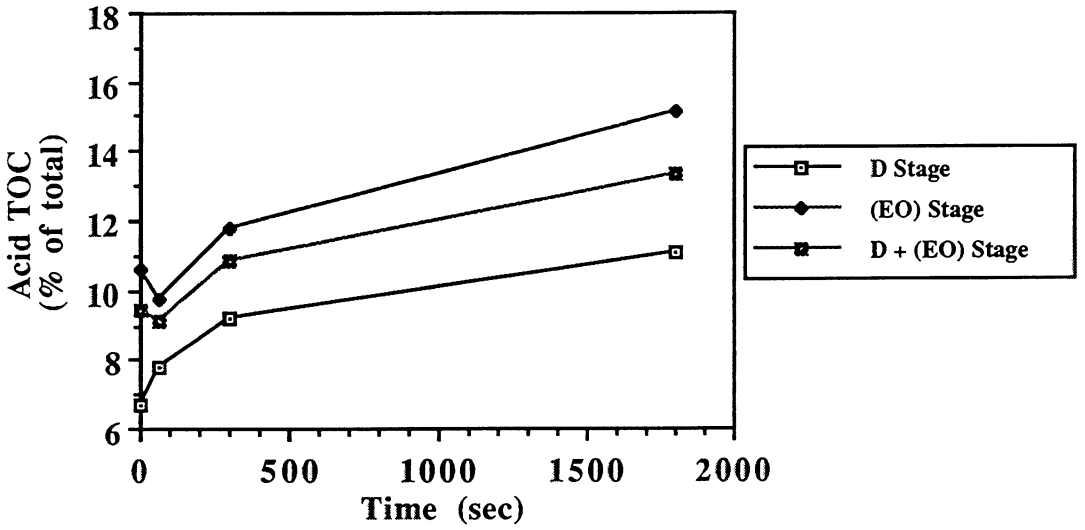


Figure 12. Acid Fraction TOC, as % of Total.

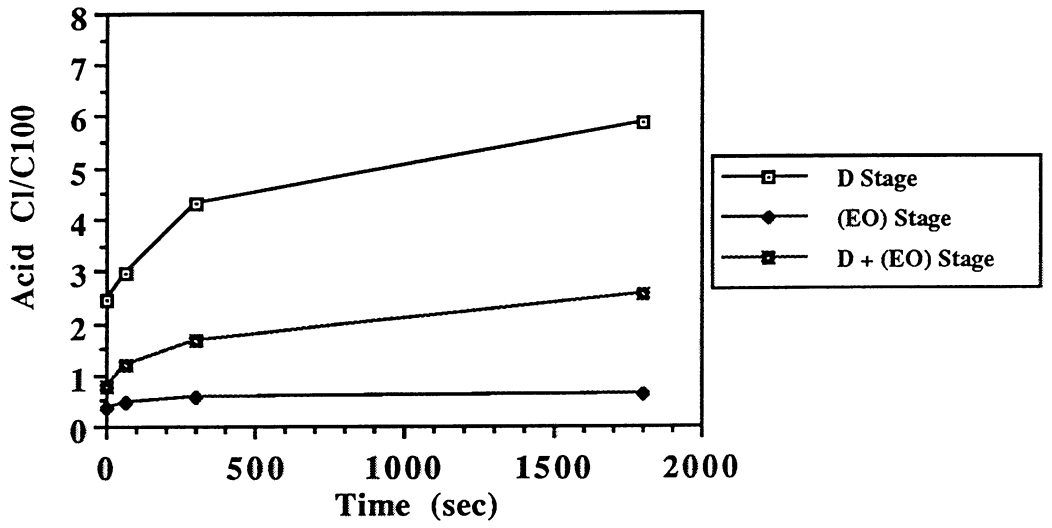


Figure 13. Acid Fraction Cl/C100.

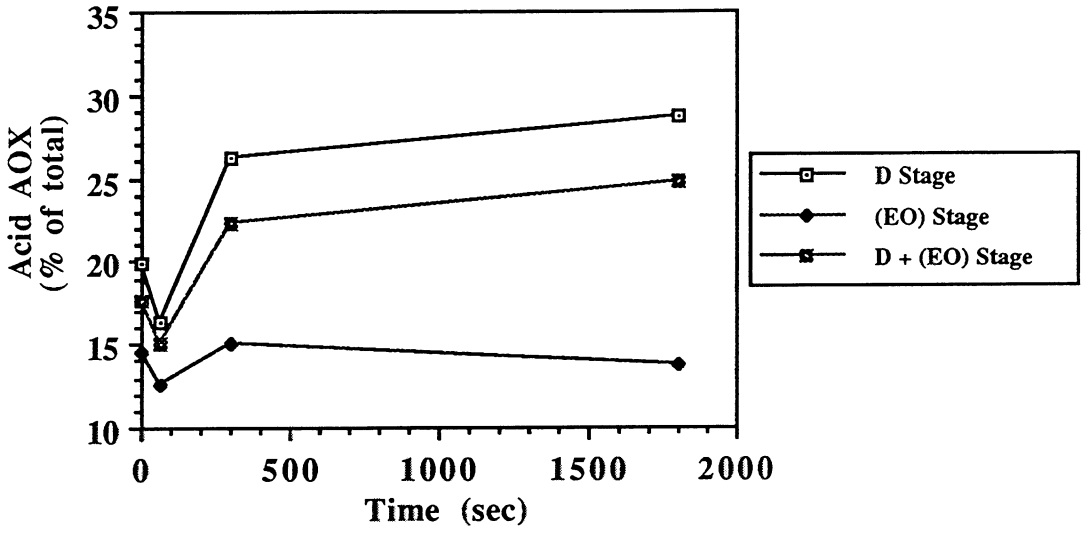


Figure 14. Acid Fraction AOX, as % of Total.

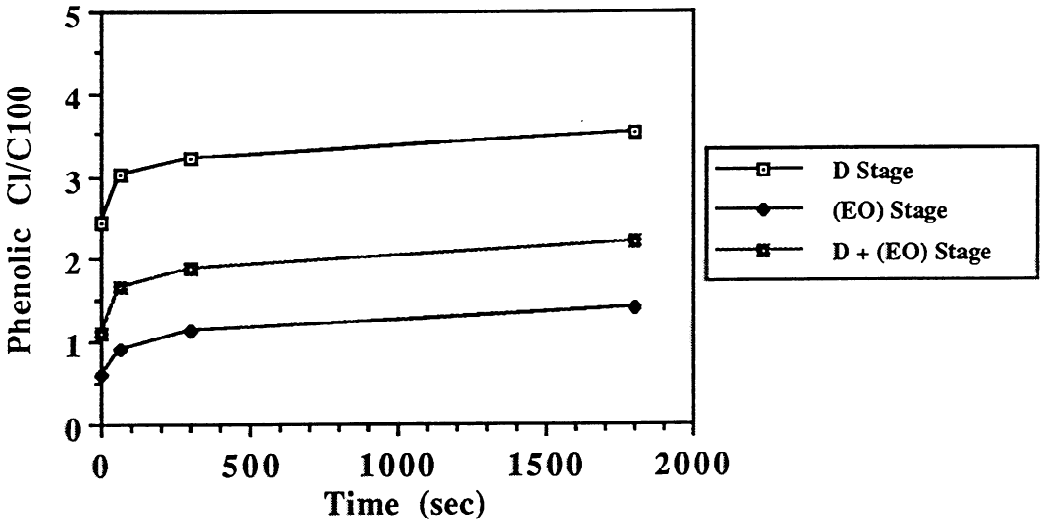


Figure 15. Phenolic Fraction Cl/C100.

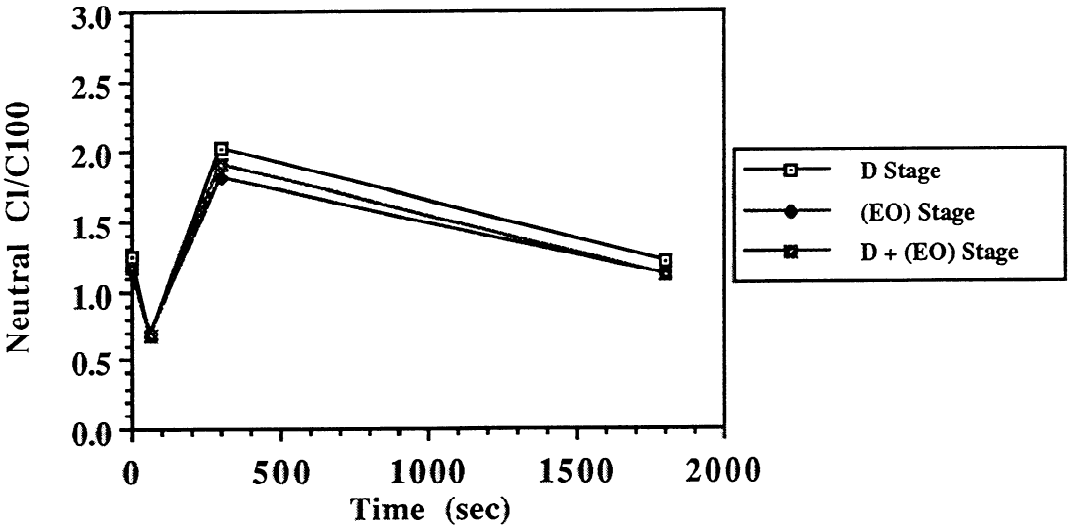


Figure 16. Neutral Fraction Cl/C100.

TABLE I. D + (EO) TOC AND KAPPA NUMBER DATA

D Stage Time, sec	D + (EO) TOC, kg/t	Kappa Number	Δ kappa	TOC/Δ kappa
3	8.56	8.23	5.87	1.46
	9.22	7.11	6.99	1.32
60	9.58	5.89	8.21	1.17
	9.31	6.56	7.54	1.23
300	10.50	5.17	8.93	1.18
	10.35	5.79	8.31	1.25
1800	11.25	4.37	9.73	1.16
	11.45	4.98	9.12	1.25

TABLE II. EFFLUENT FRACTION CODES AND DESCRIPTIONS OF FRACTIONS

Fraction Code	Description
NVW	Non-volatile, whole.
NVNEE	Non-volatile, non-ether extractable ("Hydrophilic").
NVEE II	Non-volatile, difficult to extract with ether ("Polar").
NVEE I	Non-volatile, readily ether extractable ("Ether Soluble").
NVEEA	Non-volatile, ether extractable acidic compounds ("Acids").
NVEEP	Non-volatile, ether extractable phenolic compounds ("Phenolics").
NVEEN	Non-volatile, ether extractable neutral compounds ("Neutrals").

TABLE III. WHOLE EFFLUENT AND SUMMED FRACTION CHARACTERISTICS

	D Stage Retention Time, sec			
D Stage	**3**	**60**	**300**	**1800**
TOC, kg/t	2.23 2.54	3.02 3.01	3.53 3.50	4.85 4.75
Total TOC[a], kg/t	2.45 3.03	3.13 3.14	3.42 3.74	4.84 4.95
AOX, kg/t	0.0706 0.0645	0.117 0.117	0.167 0.195	0.352 0.334
Total AOX[a], kg/t	0.0713 0.0573	0.133 0.128	0.149 0.167	0.361 0.299
Cl/C_{100}	1.07 0.86	1.31 1.31	1.61 1.88	2.46 2.38
(EO) Stage				
TOC, kg/t	6.33 6.68	6.56 6.30	6.97 6.85	6.40 6.70
Total TOC[a], kg/t	6.10 6.50	6.58 6.13	6.39 6.42	5.98 6.52
AOX, kg/t	0.0513 0.0427	0.0747 0.0614	0.0980 0.0856	0.0915 0.103
Total AOX[a], kg/t	0.0471 0.0440	0.0759 0.0667	0.0845 0.0779	0.106 0.127
Cl/C_{100}	0.27 0.22	0.39 0.33	0.48 0.42	0.48 0.52
D + (EO) Stages				
TOC, kg/t	8.56 9.22	9.58 9.31	10.5 10.4	11.3 11.5
Total TOC[a], kg/t	8.55 9.53	9.71 9.27	9.81 10.2	10.8 11.5
AOX, kg/t	0.122 0.107	0.192 0.178	0.265 0.281	0.444 0.437
Total AOX[a], kg/t	0.118 0.101	0.209 0.195	0.234 0.245	0.467 0.426
Cl/C_{100}	0.48 0.39	0.68 0.65	0.85 0.91	1.33 1.28

[a]Sum of corresponding values for volatile, hydrophilic, polar, acid, phenolic, and neutral fractions.

TABLE IV. ETHER SOLUBLE FRACTION

	D Stage Retention Time, sec			
D Stage	**3**	**60**	**300**	**1800**
TOC, kg/t	0.181 0.244	0.404 0.282	0.331 0.414	0.614 0.565
% of Total TOC	7.39 8.05	12.9 8.98	9.68 11.1	12.7 11.4
AOX, kg/t	0.0181 0.0160	0.0230 0.0250	0.0516 0.0466	0.0954 0.106
% of Total AOX	25.4 27.9	17.3 19.5	34.6 27.9	26.4 35.5
Cl/C_{100}	3.39 2.21	1.93 3.00	5.26 3.80	5.26 6.33
(EO) Stage				
TOC, kg/t	0.780 0.732	0.717 0.757	0.865 0.830	0.832 1.28
% of Total TOC	12.8 11.3	10.9 12.3	13.5 12.9	13.9 19.6
AOX, kg/t	0.0125 0.00739	0.0105 0.0108	0.0180 0.0149	0.0190 0.0217
% of Total AOX	26.5 16.8	13.8 16.2	21.3 19.1	17.9 17.1
Cl/C_{100}	0.54 0.34	0.50 0.48	0.70 0.61	0.78 0.58
D + (EO) Stages				
TOC, kg/t	0.961 0.976	1.12 1.04	1.20 1.24	1.45 1.85
% of Total TOC	11.2 10.2	11.5 11.2	12.2 12.2	13.4 16.1
AOX, kg/t	0.0306 0.0234	0.0335 0.0358	0.0696 0.0615	0.114 0.128
% of Total AOX	25.9 23.2	16.0 18.4	29.7 25.1	24.4 30.0
Cl/C_{100}	1.08 0.81	1.01 1.16	1.96 1.68	2.66 2.34

TABLE IV. ETHER SOLUBLE FRACTION

	D Stage Retention Time, sec			
D Stage	**3**	**60**	**300**	**1800**
TOC, kg/t	0.181 0244	0.404 0.282	0.331 0.414	0.614 0.565
% of Total TOC	7.39 8.05	129 8.98	9.68 11.1	127 11.4
AOX, kg/t	0.0181 0.0160	0.0230 0.0250	0.0516 0.0466	0.0954 0.106
% of Total AOX	25.4 27.9	17.3 19.5	34.6 27.9	26.4 35.5
Cl/C_{100}	339 221	1.93 3.00	526 3.80	5.26 6.33
(EO) Stage				
TOC, kg/t	0.780 0.732	0.717 0.757	0.865 0.830	0.832 128
% of Total TOC	128 11.3	10.9 123	13.5 129	13.9 19.6
AOX, kg/t	0.0125 0.00739	0.0105 0.0108	0.0180 0.0149	0.0190 0.0217
% of Total AOX	26.5 16.8	13.8 16.2	213 19.1	17.9 17.1
Cl/C_{100}	0.54 0.34	050 0.48	0.70 0.61	0.78 0.58
D + (EO) Stages				
TOC, kg/t	0.961 0.976	1.12 1.04	1.20 1.24	1.45 1.05
% of Total TOC	11.2 102	11.5 11.2	122 122	13.4 16.1
AOX, kg/t	0.0306 0.0234	0.0335 0.0358	0.06% 0.0615	0.114 0.128
% of Total AOX	25.9 23.2	16.0 18.4	29.7 25.1	24.4 30.0
Cl/C_{100}	1.08 0.81	1.01 1.16	1.96 1.68	266 234

TABLE V. POLAR FRACTION

	D Stage Retention Time, sec			
D Stage	**3**	**60**	**300**	**1800**
TOC, kg/t	0.0917 0.253	0.116 0.239	0.182 0.192	0256 0.336
% of Total TOC	3.74 5.05	3.7-I 4.43	5.32 5.11	529 6.79
AOX, kg/t	0.00622 0.00410	0.0150 0.00893	0.0193 0.0175	0.0375 0.0440
% of Total AOX	8.72 7.16	11.3 6.98	13.0 105	10.4 14.7
Cl/C_{100}	2.29 0.91	4.37 217	357 3.10	4.95 4.42
(EO) Stage				
TOC, kg/t	0591 0.527	0.619 0.722	0.782 0594	0513 0531
% of Total TOC	9.69 8.11	9.41 11.8	12.2 925	8.58 8.14
AOX, kg/t	0.00207 0.00168	0.00315 0.00282	0.00389 0.00344	0.00358 0.00335
% of Total AOX	4.39 3.82	4.15 4.23	4.60 4.42	3.91 264
Cl/C_{100}	0.12 0.11	0.17 0.13	0.17 020	024 021
D + (EO) Stages				
TOC, kg/t	0.683 0.680	0.735 0.861	0.964 0.785	0.769 0.867
% of Total TOC	7.98 7.14	7.57 929	9.83 7.70	7.12 754
AOX, kg/t	0.00829 0.00578	0.0182 0.0118	0.0232 0.0209	0.0411 0.0474
% of Total AOX	7.03 5.72	8.68 6.03	9.91 8.55	8.80 10.8
Cl/C_{100}	0.41 029	0.84 0.46	0.81 0.90	1.81 1.85

TABLE VI. HYDROPHILIC FRACTION

D Stage	D Stage Retention Time, sec			
	3	60	300	1800
TOC, kg/t	209 242	243 2.65	278 289	3.37 3.85
% of Total TOC	853 79.9	77.6 84.4	81.3 773	69.6 77.7
AOX, kg/t	0.03% 0.0352	0.0888 0.0687	0.0844 0.0903	0.149 0.156
% of Total AOX	55.5 54.6	66.8 53.7	56.6 54.1	413 52.2
Cl/C_{100}	0.64 0.49	124 0.88	1.03 1.05	1.50 137
(EO) Stage				
TOC, kg/t	4.28 5.06	5.03 4.71	4.69 4.97	4.62 4.71
% of Total TOC	70.2 77.8	76.4 76.8	73.4 77.4	773 72.2
AOX, kg/t	0.0304 0.0330	0.0522 0.0433	0.0531 0.0602	0.0810 0.0735
% of Total AOX	64.5 75.0	69.9 64.9	628 773	76.4 57.9
Cl/C_{100}	024 0.22	0.35 0.31	038 0.41	059 0.53
D + (EO) Stages				
TOC, kg/t	637 7.48	7.46 7.36	7.47 7.86	7.99 8.56
% of Total TOC	74.5 785	76.8 79.4	76.1 77.1	74.0 74.4
AOX, kg/t	0.0700 0.0682	0.141 0.122	0.138 0.252	0230 0.230
% of Total AOX	593 67.S	67.5 57.4	58.8 61.4	493 53.9
Cl/C_{100}	0.37 031	0.64 0.51	0.62 0.65	0.97 0.91

TABLE VII. ACID FRACTION

D Stage	D Stage Retention Time, sec			
	3	60	300	1800
TOC, kg/t	0.150 0219	0232 0.255	0278 0.381	0547 0533
% of Total TOC	6.12 722	7.41 8.12	8.13 10.2	11.3 10.8
AOX, kg/t	0.0137 0.0118	0.0193 0.0233	0.0397 0.0431	0.0953 0.0927
% of Total AOX	192 20.6	14.5 182	26.6 25.8	26.4 31.0
Cl/C_{100}	3.08 1.82	282 3.10	4.83 3.83	5.88 5.88
(EO) Stage				
TOC, kg/t	0.688 0.637	0.625 0.611	0.761 0.742	0.717 1.18
% of Total TOC	11.3 9.80	9.50 9.97	11.9 11.6	120 18.1
AOX, kg/t	0.00759 0.00570	0.00883 0.00899	0.0133 0.0113	0.0155 0.0165
% of Total AOX	16.1 13.0	11.6 135	15.7 14.5	14.6 13.0
Cl/C_{100}	0.37 0.30	0.48 0.50	0.59 0.52	0.73 0.47
D + (EO) Stages				
TOC, kg/t	0.838 0.856	0.857 0.866	1.04 1.12	126 1.71
% of Total TOC	9.80 8.98	8.83 9.34	10.6 11.0	11.7 14.9
AOX, kg/t	0.0213 0.0175	0.0281 0.0323	0.0530 0.0544	0.111 0.109
% of Total AOX	18.0 173	13.5 16.6	22.6 22.2	23.7 25.6
Cl/C_{100}	0.86 0.69	1.11 126	1.72 1.64	298 215

TABLE IX. NEUTRAL FRACTION

D Stage	D Stage Retention Time, sec 3	60	300	1800
TOC, kg/t	0.0495 0.0286	0.151[a] 0.0524	0.0551 0.0337	0.159 0.0538
% of Total TOC	2.02 0.944	4.82[a] 1.67	1.61 0.901	3.29 1.13
AOX, kg/t	0.00131 0.00135	0.00179[a] 0.00150	0.00265 0.00240	0.00301 0.00282
% of Total AOX	1.84 2.36	1.35[a] 1.17	1.78 1.44	0.834 0.943
Cl/C_{100}	0.89 1.59	0.40[a] 0.96	1.62 2.41	0.64 1.77
(EO) Stage				
TOC, kg/t	0.0238 0.0241	0.0566 0.0296	0.0486 0.0160	0.0267 0.0378[a]
% of Total TOC	0.390 0.371	0.860 0.483	0.761 0.249	0.446 0.580[a]
AOX, kg/t	0.000996 0.000614	0.000618 0.000908	0.00169 0.00115	0.000856 0.00135
% of Total AOX	2.11 1.40	0.927 1.36	2.00 1.48	0.808 1.06
Cl/C_{100}	1.41 0.86	0.37 1.04	1.18 2.43	1.09 1.15[a]
D + (EO) Stages				
TOC, kg/t	0.0733 0.0527	0.208 0.082	0.104 0.0497	0.186 0.0916
% of Total TOC	0.857 0.553	2.14 0.885	1.06 0.487	1.72 0.797
AOX, kg/t	0.00231 0.00196	0.00241 0.00241	0.00434 0.00355	0.00387 0.00417
% of Total AOX	1.95 1.94	1.15 1.23	1.85 1.45	0.828 0.979
Cl/C_{100}	1.07 1.26	0.39 0.99	1.41 2.41	0.70 1.54

[a]Calculated using AOX and/or TOC balances.

TABLE X. VOLATILE FRACTION

	D Stage Retention Time, sec			
D Stage	**3**	**60**	**300**	**1800**
TOC, kg/t	0.0920 0.190	0.178 0.0192	0.0898 0.216	0.475 0.139
% of Total TOC	3.76 6.27	5.69 0.611	2.63 5.78	9.81 2.81
AOX, kg/t	0.00880 0.00356	0.00756 0.0229	n.d. 0.0116	0.0724 n.d.
% of Total AOX	12.3 6.21	5.68 17.9	n.d. 6.95	20.1 n.d.
Cl/C_{100}	3.24 0.63	1.44 40.3	n.d. 1.82	5.15 n.d.
(EO) Stage				
TOC, kg/t	0.466 0.191	0.205 n.d.	0.0457 0.0456	0.0546 n.d.
% of Total TOC	7.64 2.94	3.12 n.d.	0.715 0.710	0.913 n.d.
AOX, kg/t	0.00508 0.00205	0.00986 0.00931	0.0105 n.d.	0.00311 0.000135
% of Total AOX	10.8 4.66	13.0 14.0	12.4 n.d.	2.93 0.106
Cl/C_{100}	0.37 0.36	1.62 n.d.	7.81 n.d.	1.92 n.d.
D + (EO) Stages				
TOC, kg/t	0.558 0.381	0.383 n.d.	0.136 0.262	0.530 n.d.
% of Total TOC	6.53 4.00	3.94 n.d.	1.38 2.56	4.90 n.d.
AOX, kg/t	0.0139 0.00561	0.0174 0.0322	n.d. n.d.	0.0755 n.d.
% of Total AOX	11.8 5.55	8.33 16.5	n.d. n.d.	16.2 n.d.
Cl/C_{100}	0.84 0.50	1.54 n.d.	n.d. n.d.	4.82 n.d.

n.d. - Not determined, due to no difference between whole and non-volatile whole effluent samples.